Influence of regenerable sorbents characteristics on mercury capture

C. Gómez-Giménez[1], E. García-Díez[1], D. Ballestero[2], B. Rubio[1], R. Juan[1], M.T. Izquierdo[1]
[1] Instituto de Carboquímica, ICB-CSIC. c/Miguel Luesma Castán, 4. 50018 Zaragoza. Spain.
[2] Universidad San Jorge. Autovía A23 Zaragoza-Huesca km 510. 50830 Villanueva de Gállego, Zaragoza. Spain.
mizq@icb.csic.es

Abstract

In this work, regenerable sorbents for Hg retention based on gold nanoparticles supported onto carbon monoliths structures have been developed. The aim is to test the influence of the characteristics of deposited gold on the both sorbent Hg retention capacity and efficiency, in particular Au nanoparticle size.

Regenerable sorbents were characterized by SEM-EDX, FE-SEM, ICP-OES, XPS and XRD. Performance of the different sorbents were tested in a bench scale experimental installation working at high space velocities 25000 h^{-1}, for sorbent, retention temperatures from 50ºC to 150 ºC and a Hg inlet concentration of 22 ppb.

Introduction

Main Hg anthropogenic source is the fossil fuel combustion, mostly, coal [1]. Specific technologies for mercury capture are mainly based on the use of sorbents injected in the gaseous stream for Hg capture, and subsequently retained in the particulate matter control systems, rendering new toxic residues to be controlled. Activated carbon injection (ACI) technologies require a high C:Hg ratio to achieve the desired mercury removal level (> 90%), which results in a high portion cost for sorbent material. A major problem associated with ACI technology is that the commercial value of fly ash is sacrificed due to its mixing with contaminated activated carbon powder and the generation of high amount of toxic residue.

Carbon filter beds before stack present problems associated to the low affinity between non-treated carbons and elemental mercury as well as the pressure drop in the fixed bed. High efficiency sulphur doped carbons are used for Hg retention on fixed beds, but the problem of toxic wastes still remains.

Regenerable sorbents can accomplish high mercury retention as well as balance cost because of this regenerability. Elemental mercury amalgamated with gold. This amalgam is extremely stable at room temperature and decomposes at higher temperature leaving clean gold ready for further capture [2, 3]. In order to capture trace amounts of mercury it is necessary to have the gold in a form of large surface areas [4]. However, metal monolayer tends to aggregate into larger islands in micrometer sizes after repetitive Hg exposure and heating, which could lead to inefficient mercury capture [2, 4, 5]. The efficiency of the Au for the retention of mercury would be enhanced if nanometric particulate sizes of the metal could be achieved.

In this work two Au/C sorbents prepared by two different methodologies were tested for mercury capture at different temperatures of operation in order to gain insight about the influence of the characteristics of gold deposited on Hg capture performance.

Experimental

A commercial carbon monolith with honeycomb structure was used as support for gold deposition. This support was used without treatment for direct gold deposition or treated with HNO_3 (acid concentration 65%, 80ºC, 4h) for colloidal gold deposition.

The first method for gold deposition consists of the direct reduction of the gold salt by the own carbon material of the support. The salt used for gold deposition was $HAuCl_4$•3H2O. A solution of 40 mg/l of salt in ethanol/water (1:1 v/v) was forced to pass through the channels of the carbon monolith to try to achieve a homogeneous deposition of gold along the channels of the monolithic supports. The contact time of the dissolution passing through the channels of the monolith was 30 min. The second method is based on the formation of colloidal gold [6] with the modification of [7] . During the formation of colloidal gold, citrate anion acts as reducing agent of the gold salt and as protector of the gold sol formed preventing its aggregation. The colloidal solution of gold is forced to pass through the channels, with a total contact time between channels of the monoliths and the colloidal solution of 40 min. After gold deposition distilled water was pumped through the channels of the sorbents to remove the spare gold dissolution. Sorbents were vacuum dried at 30ºC for 30 min. Sorbents were finally undergone to a reducing thermal treatment (TTR) at 300ºC in a flow containing 4% H_2 during 1 h. Sorbents obtained by direct reduction of gold or by deposition of colloidal gold were labelled as MC-Au-red and MC-Au-col, respectively.

Sorbents were characterized by different techniques. The bulk Au content of the sorbents was obtained by Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES). The surface Au content was determined by Scanning Electron Microscopy with Energy Dispersive X-ray Spectroscopy (SEM-EDX). The gold nanoparticle size distribution was obtained by image analysis (free software “Image J”) of electron micrographs taken by Scanning Electron Microscopy with Field-Emission (FE-SEM) technique. The oxidation states of gold were analyzed by X-ray Photoelectron Spectroscopy (XPS).
After mercury retention, some sorbents were characterized by XPS, in order to detect possible changes in Au oxidation state and X-ray Diffraction (XRD) in order to test crystal modification of Au by Au-Hg alloy formation.

A bench scale installation (Figure 1) was used to determine the efficiency of the sorbents for the capture of mercury and the maximum retention capacity. A permeation tube for mercury gives the desired Hg concentration. The mercury is analyzed on-line with an elemental mercury analyzer (VM3000). Moreover, the installation is provided with a tail-end train of flasks to allow the capture the mercury as well as its speciation (in the case of evidences of oxidation under the experimental conditions). The installation is built up with Teflon pipes and pieces (in the part of the installation where Hg is present) to prevent possible mercury attack to steel. More details of the experimental installation are given elsewhere [3].

For the study of the influence of temperature on Hg capture, breakthrough curves were obtained at space velocity $7x10^8$ h^{-1} (referred to the active phase), temperatures from 50ºC to 150ºC and Hg inlet concentration of 22 ppb in N_2. It was considered that saturation is reached at 95% saturation. Moreover, the amount of Hg retained at 20% and 80% of breakthrough

was calculated from the integration of the breakthrough curve. The efficiency of Hg retention was calculated as the ratio between the amount of Hg retained by the sorbents at either 20% or 80% of saturation and the total amount of Hg fed into the reaction during this time. Some experiments were repeated to test reproducibility. Some of the exhausted sorbents after Hg capture were analyzed for Hg content in an automated mercury analyzer (AMA) from Leco, and the results were compared with those obtained by breakthrough curve integration.

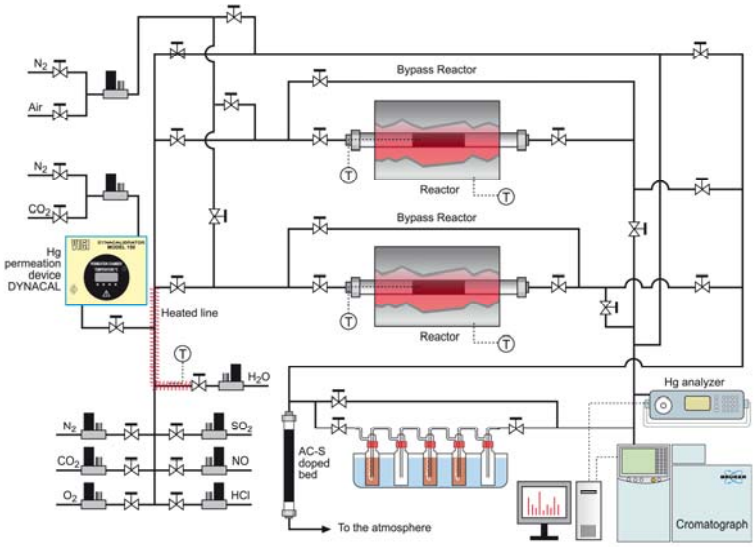

Figure 1. Experimental installation for Hg mercury tests.

Results and Discussion

The gold content in the bulk sorbent was determined by ICP-OES and it was 0.11% for sorbent MC-Au-red and 0.035% for sorbent MC-Au-col. According to XPS studies, gold is mainly present as Au^0 for both sorbents prepared.

The study of the distribution of gold along the monolith channels was carried out by SEM-EDX. Monoliths were longitudinal sectioned in order to determine the Au distribution along the channels. Seven measurement of gold content along each channel was carried out and an appropriate homogeneity of Au content was found. Moreover, different channels of a monolith and different monoliths were tested to obtain a representative value for Au surface content. The surface gold content from SEM-EDX for sorbent MC-Au-red was 3.96% and for MC-Au-col was 1.92%.

In order to obtain the gold particle size distribution on the sorbents, several micrographs were taken by FE-SEM in backscattering mode. These micrographs were analyzed by image analysis using Image J free software. Average particle size (Feret's diameter) was 23 nm for sorbent MC-Au-red (diameter is 173 nm if smallest particles <10 nm are excluded because they just have a small contribution, 2%, to the area covered by individual particles) and 30 nm for sorbent MC-Au-col.

Figure 2 shows breakthrough curves for MC-Au-red and MC-Au-col sorbent at different temperatures and initial Hg concentration in N_2 of 200 $\mu g/m^3$. It can be observed that breakthrough times are larger for MC-Au-red sorbent than that for MC-Au-col. On the other hand, it seems that temperature influences in more extent on MC-Au-col breakthrough curve.

This fact can be attributed to the different Au content of both sorbents, as can be deduced in Figure 3. Both sorbents can reach similar amounts of Hg captured by Au content despite their differences in Au particle size. This fact seems a contradiction because there is an overwhelming evidence of the dependence of Au particle size and its characteristics related to the defects on the crystal structure. However, in present case the average particle size is far from that reported in the literature, less than 6 nm, which maximize the effect of particle size on structural defects of the Au crystal [8]. In present case, the independence of particle size on the Hg retention could be explained as follows: the high Au particle size for both sorbents does not make differences on Au crystal structure and consequently, no differences are found in Hg capture performance.

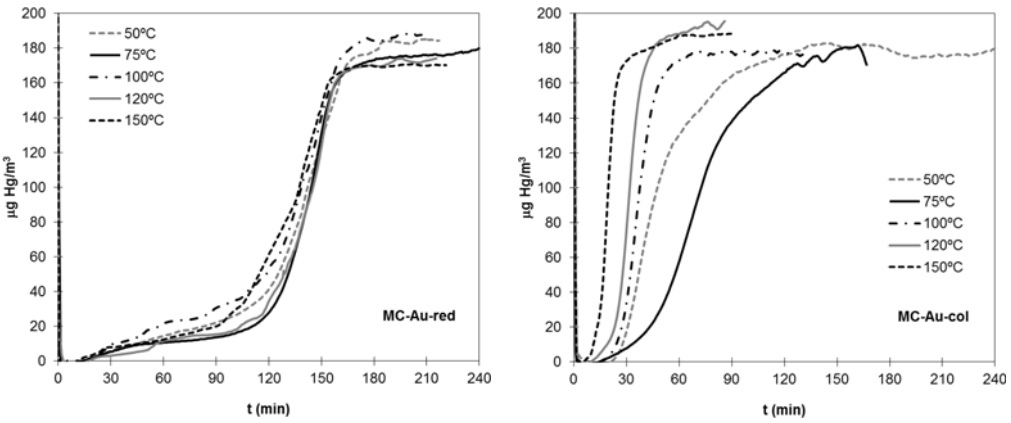

Figure 2. Hg breakthrough curves (initial Hg concentration 200 µg/m^3 in N_2).

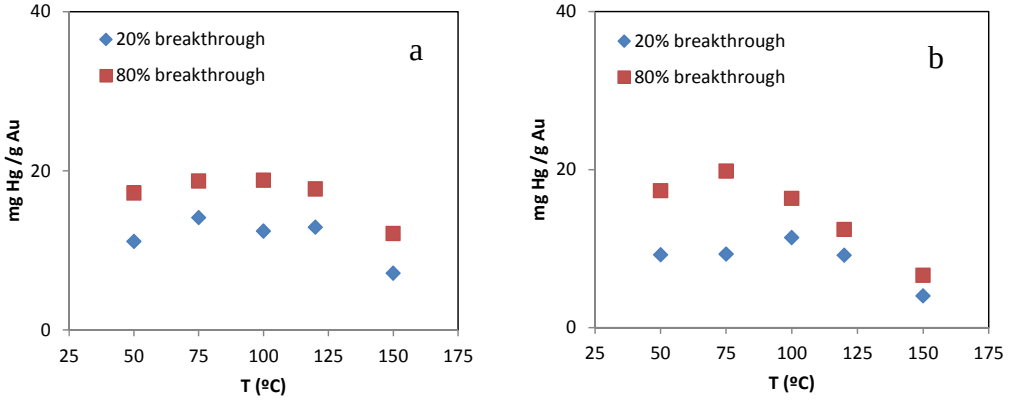

Figure 3. Amount of Hg captured at 20% and 80% breakthrough for sorbent a) MC-Au-red and b) MC-Au-col.

At 20% breakthrough the Hg capture efficiencies are around 85% for all the temperatures studied. The highest temperature used for Hg retention gives low Hg retention capacity. This fact can be related with the low temperature needed to regenerate the sorbents, which was 220ºC [3]. Hg evolution started near 180ºC, which is close enough to the retention temperature of 150ºC. This effect is more pronounced for sorbent MC-Au-col, because the Hg evolution in Hg-TPD experiments a slightly lower temperature than that for sorbent MC-Au-red.

After Hg exposition, both sorbents were characterized in order to follow possible changes in gold. The exposition to mercury has not changed the XRD pattern of gold. As it was previously discussed [3] the mercury capture on the Au/C sorbent is based on the amalgam

mechanism, so displacement of Au peaks was expected because of the formation of Au-Hg amalgam [9]. However, in present case the relation Hg/Au is low for both sorbents and this should be the reason of no new peaks appearing and no intensity of peaks decreasing.

Acknowledgements

The financial support from Spanish Ministry of Science and Innovation and European Regional Development Funds (ref: ENE2011-23412) is duly recognized. C. Gómez-Giménez wants to thank CSIC and European Regional Development Funds for JAE grant.

References

[1] The Global Atmospheric Mercury Assesment: Sources, Emissions and Transport., in, UNEP-Chemicals, Geneva, Switzerland, 2008.
[2] R. Nowakowski, T. Kobiela, Z. Wolfram, R. Dus, Atomic force microscopy of Au/Hg alloy formation on thin Au films, Applied Surface Science, 115 (1997) 217-231.
[3] M. Izquierdo, D. Ballestero, R. Juan, E. Garcia-Diez, B. Rubio, C. Ruiz, M. Pino, Tail-end Hg capture on Au/carbon-monolith regenerable sorbents, Journal of Hazardous Materials, 193 (2011) 304-310.
[4] F.H. Schaedlich, D.R. Schneeberger, Cartridge for Collection of a Sample by Adsorption onto a Solid Surface, in: Patent nº US 5660795, 1997.
[5] C. Battistoni, E. Bemporad, A. Galdikas, S. Kaciulis, G. Mattogno, S. Mickevicius, V. Olevano, Interaction of mercury vapour with thin films of gold, Applied Surface Science, 103 (1996) 107-111.
[6] J. Turkevich, P.C. Stevenson, J. Hillier, A study of the nucleation and growth processes in the synthesis of colloidal gold., Discussions of the Faraday Society, (1951) 55-75.
[7] T. Muangnapoh, N. Sano, S.-I. Yusa, N. Viriya-empikul, T. Charinpanitkul, Facile strategy for stability control of gold nanoparticles synthesized by aqueous reduction method, Current Applied Physics, 10 (2010) 708-714.
[8] S. Schimpf, M. Lucas, C. Mohr, U. Rodemerck, A. Bruckner, J. Radnik, H. Hofmeister, P. Claus, Supported gold nanoparticles: in-depth catalyst characterization and application in hydrogenation and oxidation reactions, Catalysis Today, 72 (2002) 63-78.
[9] T. Kobiela, B. Nowakowski, R. Dus, The influence of gas phase composition on the process of Au-Hg amalgam formation, Applied Surface Science, 206 (2003) 78-89.